



⑫

EUROPEAN PATENT APPLICATION

⑳ Application number : **92304144.6**

㉑ Int. Cl.⁵ : **C07C 253/24, C07C 255/08**

㉒ Date of filing : **08.05.92**

㉓ Priority : **09.05.91 JP 104382/91**

㉔ Date of publication of application :
11.11.92 Bulletin 92/46

㉕ Designated Contracting States :
DE FR GB IT NL

㉖ Applicant : **MITSUBISHI KASEI CORPORATION**
5-2, Marunouchi 1-chome Chiyoda-ku
Tokyo (JP)

㉗ Inventor : **Ushikubo, Takashi**
1-1-66, Tachibanadai, Midori-ku
Yokohama-shi, Kanagawa-ken (JP)

Inventor : **Oshima, Kazunori**
2-32-4, Narusedai
Machida-shi, Tokyo (JP)

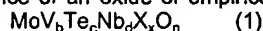
Inventor : **Umezawa, Tiaki**
1-1552-1, Miyamado-cho
Yokkaichi-shi, Mie-ken (JP)

Inventor : **Kiyono, Ken-ichi**
2-12-2, Ogawa
Machida-shi, Tokyo (JP)

㉘ Representative : **Hayes, Adrian Chetwynd (GB)**
et al
J. A. Kemp & Co. 14 South Square Gray's Inn
GB-London WC1R 5EU (GB)

㉙ **Process for producing nitriles.**

㉚ A process for producing a nitrile, which comprises subjecting an alkane and ammonia in the gaseous state to catalytic oxidation in the presence of an oxide of empirical formula :



wherein :

X is at least one of Mg, Ca, Sr, Ba, Al, Ga, Ti, In, Zr, Hf, Ta, Cr, Mn, W, Fe, Ru, Co, Rh, Ni, Pd, Pt, Zn, Sn, Pb, As, Sb, Bi, La and Ce ;

b is from 0.01 to 1.0 ;

c is from 0.01 to 1.0 ;

d is from 0 to 1.0 ;

x is from 0.0005 to 1.0 ; and

n is a number such that the total valency of the metal elements is satisfied.

The present invention relates to a process for producing nitriles.

Nitriles such as acrylonitrile and methacrylonitrile have been industrially produced as important intermediates for the preparation of, for example, fibers, synthetic resins and synthetic rubbers. The most popular method for producing such nitriles is to subject an olefin such as propylene or isobutene to a reaction with ammonia and oxygen in the presence of a catalyst in a gaseous phase at a high temperature.

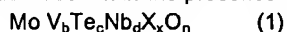
On the other hand, in view of the price difference between propane and propylene or between isobutane and isobutene, attention has been drawn to developing a method for producing acrylonitrile or methacrylonitrile by a so-called ammooxidation reaction method wherein a lower alkane, such as propane or isobutane, is used as starting material. This lower alkane is catalytically reacted with ammonia and oxygen in a gaseous phase in the presence of a catalyst. Catalysts which have been used are a Mo-Bi-P-O catalyst (JP-A-16887/1973), a V-Sb-O catalyst (JP-A-33783/1972, JP-B-23016/1975 and JP-A-268668/1989), a Sb-U-V-Ni-O catalyst (JP-B-14371/1972), a Sb-Sn-O catalyst (JP-B-28940/1975), a V-Sb-W-P-O catalyst (JP-A-95439/1990), a catalyst obtained by mechanically mixing a V-Sb-W-O oxide and a Bi-Ce-Mo-W-O oxide (JP-A-38051/1989) and a Mo-V-Te-Nb-O catalyst (JP-A-257/1990 and US-A-5,049,692).

However, none of these methods provides a fully satisfactory yield of the nitriles. In order to improve the yield it has been proposed to add a small amount of an organic halide, an inorganic halide or a sulfur compound, or to add water to the reaction system. However, the former method has a problem of possible corrosion of the reaction apparatus, while the latter method has a problem of formation of by-products by side reactions or a problem of their treatment. Thus, each method has a practical problem in industrial application.

Methods using conventional catalysts other than the Mo-V-Te-Nb-O catalyst usually require a very high reaction temperature of at least 500°C. Therefore, such methods are disadvantageous, for example in terms of the reactor material and production cost.

We have surprisingly found it possible to produce a desired nitrile in a better yield than conventional methods at a relatively low temperature of from 400 to 450°C without adding a halide or water to the reaction system, by subjecting the alkane and ammonia in the gaseous state to catalytic oxidation in the presence of an oxide comprising molybdenum (Mo), vanadium (V), tellurium (Te), niobium (Nb) and certain other metals, or an oxide comprising molybdenum (Mo), vanadium (V), tellurium (Te) and certain other metals, as a complex oxide.

The present invention provides a process for producing a nitrile, which comprises subjecting an alkane and ammonia in the gaseous state to catalytic oxidation in the presence of an oxide of empirical formula:



wherein:

X is at least one of Mg, Ca, Sr, Ba, Al, Ga, Ti, In, Zr, Hf, Ta, Cr, Mn, W, Fe, Ru, Co, Rh, Ni, Pd, Pt, Zn, Sn, Pb, As, Sb, Bi, La and Ce;

b is from 0.01 to 1.0;

c is from 0.01 to 1.0;

d is from 0 to 1.0;

x is from 0.0005 to 1.0; and

n is a number such that the total valency of the metal elements is satisfied.

X is particularly preferably Mg, Ca, Ba, Al, Ta, Cr, Mn, W, Fe, Co, Ni, Pd, Zn, Sn, Sb or Bi. It is preferred that b is from 0.1 to 0.6, c is from 0.05 to 0.4 and x is from 0.05 to 0.6.

Such a complex oxide may be prepared by the following method.

For example, in the case of $\text{MoV}_b\text{Te}_c\text{Nb}_d\text{Sn}_x\text{O}_n$, added sequentially to an aqueous solution containing a predetermined amount of ammonium metavanadate, are an aqueous solution of tin oxalate, an aqueous solution of telluric acid, an aqueous solution of ammonium niobium oxalate and an aqueous solution of ammonium paramolybdate in such amounts that the atomic ratios of the respective metal elements would fall in the ranges specified above, and the mixture is evaporated to dryness at a temperature of from 100 to 200°C, and the dried product is calcined at a temperature of from 350 to 700°C to obtain a desired complex oxide.

The materials for the complex oxide are not limited to the ones mentioned above. For example, V_2O_5 , V_2O_3 , VOCl_3 or VCl_4 may be used instead of ammonium metavanadate, and tin nitrate, tin acetate, SnCl_2 , SnCl_4 , SnO or SnO_2 may be used instead of the above-mentioned tin oxalate. Likewise, TeO_2 may be used instead of telluric acid; NbCl_5 , Nb_2O_5 or niobic acid may be used instead of ammonium niobium oxalate; and MoO_3 , MoCl_5 , phosphomolybdic acid or silicomolybdic acid may be used instead of ammonium paramolybdate. Further, it is possible to use a heteropolyacid which contains mixed-coordinate molybdenum and vanadium, such as molybdovanadophosphoric acid.

Such a complex oxide may be used alone. However, it may be used together with a conventional carrier such as silica, alumina, titania, aluminosilicate or diatomaceous earth. Further, depending upon the scale or system of the reaction, it may be molded into a proper shape and particle size.

The process of the present invention is a process for producing a nitrile by subjecting an alkane to a gas

phase catalytic oxidation reaction with ammonia in the presence of the above complex oxide.

In the present invention, the alkane as the starting material is not particularly limited and may, for example, be methane, ethane, propane, butane, isobutane, pentane, hexane, heptane or cyclohexane. However, in view of the industrial application of nitriles to be produced, it is particularly preferred to employ a lower alkane having from 1 to 4 carbon atoms, particularly propane or isobutane.

The detailed mechanism of the oxidation reaction of the present invention is not clearly understood. However, the oxidation reaction is conducted by the oxygen atoms present in the above complex oxide or by the molecular oxygen present in the feed gas. When molecular oxygen is incorporated in the feed gas, the oxygen may be pure oxygen gas. However, since the purity is not required, it is usually economical to use an oxygen-containing gas such as air. When no oxygen is incorporated in the feed gas, it is advisable to supply the alkane-ammonia gas mixture and the oxygen-containing gas alternately to prevent deterioration of the complex oxide by reduction, or to adopt a method wherein by means of a mobile bed type reactor, the complex oxide is continuously supplied to an oxidative regenerator so that it will be regenerated for reuse.

The present invention will be described in further detail with respect to a case where propane is used as the alkane and air is used as the oxygen source. The proportion of air to be supplied for the reaction is important with respect to the selectivity for the resulting acrylonitrile. Namely, high selectivity for acrylonitrile is obtained when air is supplied within a range of at most 25 mols, particularly from 1 to 15 mols per mol of propane. The proportion of ammonia to be supplied for the reaction is preferably within a range of from 0.2 to 5 mols, particularly from 0.5 to 3 mols, per mol of propane. This reaction may usually be conducted under atmospheric pressure, but may be conducted under a slightly increased pressure or a slightly reduced pressure.

The process of the present invention can be conducted at a temperature of e.g. from 380 to 480°C, which is lower than the temperature for conventional ammooxidation of alkanes. More preferably, the temperature is from 400 to 450°C. The gas space velocity SV in the gas phase reaction is usually within a range of from 100 to 10,000 hr⁻¹, preferably from 300 to 2,000 hr⁻¹. As a diluent gas for adjusting the space velocity and the oxygen partial pressure, an inert gas such as nitrogen, argon or helium can be employed. When ammooxidation of propane is conducted by the method of the present invention, in addition to acrylonitrile, carbon monoxide, carbon dioxide, acetonitrile, hydrocyanic acid, acrolein, etc. will form as by-products, but their amounts are very small.

Now, the present invention will be described in further detail with reference to Examples and Comparative Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

In the following Examples and Comparative Examples, the conversion (%), the selectivity (%) and the yield (%) are shown by the following formulas, respectively:

$$\text{Conversion of alkane (\%)} = \frac{\text{mols of consumed alkane}}{\text{mols of supplied alkane}} \times 100$$

$$\text{Selectivity of objective nitrile (\%)} = \frac{\text{mols of objective nitrile obtained}}{\text{mols of consumed alkane}} \times 100$$

$$\text{Yield of objective nitrile (\%)} = \frac{\text{mols of supplied alkane}}{\text{mols of objective nitrile obtained}} \times 100$$

EXAMPLE 1

A complex oxide having an empirical formula Mo₁V_{0.4}Te_{0.2}Nb_{0.1}Mn_{0.1}O_n was prepared as follows.

In 117 ml of warm water, 4.21 g of ammonium metavanadate was dissolved, and 4.13 g of telluric acid, 15.89 g of ammonium paramolybdate and 3.99 g of manganese acetate tetrahydrate were sequentially added thereto to obtain a uniform aqueous solution. Further, 3.99 g of ammonium niobium oxalate was dissolved in 17.9 ml of water and added thereto. The obtained aqueous solution was evaporated to dryness at about 150°C to obtain a solid material.

This solid material was molded into a tablet of 5 mm in diameter and 3 mm in length by a tableting machine, followed by pulverization and sieving to obtain a powder of from 16 to 28 mesh. The powder was calcined at a temperature of 350°C, and then used for the reaction.

0.5 ml of the complex oxide thus obtained, was charged into a reactor. Then, a gas phase catalytic reaction was conducted at a reaction temperature of 440°C and at a space velocity SV of 1000 hr⁻¹ by supplying a feed gas in a molar ratio of propane:ammonia:air = 1:1.2:10. The results are shown in Table 1.

EXAMPLE 2

A complex oxide was prepared in the same manner as in Example 1 except that 2.24 g of nickel acetate tetrahydrate was used instead of manganese acetate tetrahydrate. The composition of the obtained complex

oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{Ni}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 440°C). The results are shown in Table 1.

5 EXAMPLE 3

A complex oxide was prepared in the same manner as in Example 1 except that 1.34 g of magnesium oxalate dihydrate was used instead of manganese acetate tetrahydrate. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{Mg}_{0.1}\text{O}_n$.

10 Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 450°C). The results are shown in Table 1.

EXAMPLE 4

15 A complex oxide was prepared in the same manner as in Example 1 except that 3.85 g of ammonium iron oxalate trihydrate was used instead of manganese acetate tetrahydrate. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{Fe}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 420°C). The results are shown in Table 1.

20

EXAMPLE 5

A complex oxide was prepared in the same manner as in Example 1 except that 2.13 g of tin acetate tetrahydrate was used instead of manganese acetate tetrahydrate. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{Sn}_{0.1}\text{O}_n$.

25

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 440°C, SV: 2000 hr⁻¹). The results are shown in Table 1.

EXAMPLE 6

30

A complex oxide was prepared in the same manner as in Example 1 except that 0.24 g of cobalt acetate tetrahydrate was used instead of manganese acetate tetrahydrate. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{Co}_{0.1}\text{O}_n$.

35

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 420°C, SV: 500 hr⁻¹). The results are shown in Table 1.

COMPARATIVE EXAMPLE 1

40

A complex oxide was prepared in the same manner as in Example 1 except that the niobium and manganese were not used. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 400°C, SV: 500 hr⁻¹ and 1000 hr⁻¹). The results are shown in Table 1.

45

COMPARATIVE EXAMPLE 2

A complex oxide was prepared in the same manner as in Example 1 except that the manganese component was not used. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{O}_n$.

50

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 420°C, SV: 500 hr⁻¹, and reaction temperature: 440°C, SV: 1000 hr⁻¹). The results are shown in Table 1.

55

Table 1

	Complex oxide (atomic ratio)	SV (hr ⁻¹)	Temp (°C)	Conversion of propane (%)	Selectivity for acrylonitrile (%)	Yield of acrylonitrile (%)
Example 1	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} Mn _{0.1} O _n	1000	440	57.5	41.5	23.9
Example 2	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} Ni _{0.1} O _n	1000	440	59.1	37.5	22.1
Example 3	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} Mg _{0.1} O _n	1000	450	48.5	43.5	21.1
Example 4	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} Fe _{0.1} O _n	1000	420	48.4	35.0	16.9
Example 5	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} Sn _{0.1} O _n	2000	440	57.8	43.6	25.2
Example 6	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} Co _{0.1} O _n	500	420	46.7	39.1	18.2
Comparative Example 1	Mo ₁ V _{0.4} Te _{0.2} O _n	500	400	14.5	24.1	3.5
	Mo ₁ V _{0.4} Te _{0.2} O _n	1000	400	9.5	24.2	2.3
Comparative Example 2	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} O _n	500	420	43.2	27.1	11.7
	Mo ₁ V _{0.4} Te _{0.2} Nb _{0.1} O _n	1000	440	48.8	34.2	16.7

EXAMPLE 7

A complex oxide having the empirical formula $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Fe}_{0.1}\text{O}_n$ was prepared as follows.

In 65 ml of warm water, 2.34 g of ammonium metavanadate was dissolved, and 2.3 g of telluric acid, 8.83 g of ammonium paramolybdate and 2.14 g of ammonium ferric oxalate were sequentially added thereto to obtain a uniform aqueous solution. This solution was heated and then evaporated to dryness at about 150°C to obtain a solid material.

This solid material was molded into a tablet of 5 mm in diameter and 3mm in length by a tableting machine, followed by pulverization and sieving to obtain a powder of from 16 to 28 mesh. The powder was calcined at 350°C for 3 hours under an air stream, and then used for the reaction.

0.5 ml of the complex oxide thus obtained, was charged into a reactor, and a gas phase catalytic reaction was conducted at a reaction temperature of 420°C at a space velocity SV 500 hr⁻¹ by supplying a feed gas in a molar ratio of propane:ammonia:air = 1:1.2:10. The results are shown in Table 2.

EXAMPLE 8

A complex oxide was prepared in the same manner as in Example 7 except that 1.28 g of magnesium nitrate hexahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Mg}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 420°C). The results are shown in Table 2.

EXAMPLE 9

A complex oxide was prepared in the same manner as in Example 7 except that 1.88 g of aluminum nitrate trihydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Al}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 420°C). The results are shown in Table 2.

EXAMPLE 10

A complex oxide was prepared in the same manner as in Example 7 except that 1.18 g of calcium nitrate tetrahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ca}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 1 (reaction temperature: 400°C). The results are shown in Table 2.

EXAMPLE 11

A complex oxide was prepared in the same manner as in Example 7 except that 1.31 g of barium nitrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ba}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 400°C). The results are shown in Table 2.

EXAMPLE 12

A complex oxide was prepared in the same manner as in Example 7 except that 0.87 g of antimony chloroxide was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Sb}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 400°C). The results are shown in Table 2.

EXAMPLE 13

A complex oxide was prepared in the same manner as in Example 8 except that 2.43 g of bismuth nitrate pentahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex

oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Bi}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 8 (reaction temperature: 400°C). The results are shown in Table 2.

5 EXAMPLE 14

A complex oxide was prepared in the same manner as in Example 7 except that 1.49 g of zinc nitrate hexahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Zn}_{0.1}\text{O}_n$.

10 Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 420°C). The results are shown in Table 2.

EXAMPLE 15

15 A complex oxide was prepared in the same manner as in Example 7 except that 4.01 g of tantalum oxalate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 420°C). The results are shown in Table 2.

20

EXAMPLE 16

A complex oxide was prepared in the same manner as in Example 7 except that 2.32 g of ammonium metatungstate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{W}_{0.1}\text{O}_n$.

25

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 400°C). The results are shown in Table 2.

EXAMPLE 17

30

A complex oxide was prepared in the same manner as in Example 7 except that 1.44 g of manganese nitrate hexahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Mn}_{0.1}\text{O}_n$.

35

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 400°C). The results are shown in Table 2.

EXAMPLE 18

40

A complex oxide was prepared in the same manner as in Example 7 except that 1.46 g of cobalt nitrate hexahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Co}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 420°C). The results are shown in Table 2.

45

EXAMPLE 19

A complex oxide was prepared in the same manner as in Example 7 except that 1.45 g of nickel nitrate hexahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ni}_{0.1}\text{O}_n$.

50

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7 (reaction temperature: 420°C). The results are shown in Table 2.

EXAMPLE 20

55

A complex oxide was prepared in the same manner as in Example 7 except that 2.00 g of chromium nitrate nonahydrate was used instead of ammonium ferric oxalate. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Cr}_{0.1}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same

manner as in Example 1 (reaction temperature: 420°C). The results are shown in Table 2.

COMPARATIVE EXAMPLE 3

5 A complex oxide was prepared in the same manner as in Example 7 except that no iron component was used. The empirical composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and air in the same manner as in Example 7. The results are shown in Table 2.

Table 2

	Complex oxide (atomic ratio)	Temp (°C)	Conversion of propane (%)	Yield of acrylo- nitrile (%)
Example 7	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Fe}_{0.1}\text{O}_n$	420	52.2	16.0
Example 8	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Mg}_{0.1}\text{O}_n$	420	53.5	18.1
Example 9	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Al}_{0.1}\text{O}_n$	420	52.7	17.6
Example 10	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ca}_{0.1}\text{O}_n$	400	47.2	14.0
Example 11	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ba}_{0.1}\text{O}_n$	400	46.3	14.0
Example 12	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Sb}_{0.1}\text{O}_n$	400	43.0	15.7
Example 13	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Bi}_{0.1}\text{O}_n$	400	47.6	17.3
Example 14	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Zn}_{0.1}\text{O}_n$	420	52.7	16.6
Example 15	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ta}_{0.1}\text{O}_n$	420	46.8	17.5
Example 16	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{W}_{0.1}\text{O}_n$	400	40.8	15.4
Example 17	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Mn}_{0.1}\text{O}_n$	400	50.2	15.9
Example 18	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Co}_{0.1}\text{O}_n$	420	51.4	17.0
Example 19	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ni}_{0.1}\text{O}_n$	420	51.6	15.8
Example 20	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Cr}_{0.1}\text{O}_n$	420	50.6	16.4
Compara- tive Example 3	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_n$	420	14.5	3.5

EXAMPLES 21 to 23

55 Using complex oxides prepared in the same manner as in Examples 7, 13 and 17, respectively, gas phase catalytic reactions of propane and ammonia were conducted. In each case, 0.5 ml of the complex oxide was charged into a reactor, and the gas phase catalytic reaction was conducted at a reaction temperature of 400°C at a space velocity SV of 1000 hr⁻¹ by supplying a feed gas in a molar ratio of propane:ammonia:air = 1:1.2:10.

The results are shown in Table 3.

COMPARATIVE EXAMPLE 4

- 5 Using a composite oxide of the empirical composition $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_x$ prepared in the same manner as in Comparative Example 3, a gas phase catalytic reaction was conducted under the same conditions as in Example 21. The results are shown in Table 3.

Table 3

	Complex oxide (atomic ratio)	Conversion of propane (%)	Yield of acrylonitrile (%)
Example 21	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Fe}_{0.1}\text{O}_n$	43.6	15.1
Example 22	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Bi}_{0.1}\text{O}_n$	43.6	16.6
Example 23	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Mn}_{0.1}\text{O}_n$	42.2	15.4
Comparative Example 4	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_n$	9.5	2.3

EXAMPLE 24

- 0.2 cc of the oxide obtained in Example 7 was charged into a reactor, and a gas phase catalytic reaction was conducted at a reaction temperature of 440°C at a space velocity of 2000 hr⁻¹ by supplying a reaction gas in a molar ratio of propane:ammonia:nitrogen = 10:1.6:11.2 for 3 minutes, i.e. in the absence of oxygen. The results are shown in Table 4.

EXAMPLE 25

- A complex oxide was prepared in the same manner as in Example 7 except that 24.86 g of ammonium titanium oxalate was used instead of ammonium ferric oxalate. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ti}_{0.4}\text{O}_n$.

Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and nitrogen in the same manner as in Example 24. The results are shown in Table 4.

EXAMPLE 26

- A complex oxide was prepared in the same manner as in Example 7 except that 0.593 g of stannic oxalate was used instead of ammonium ferric oxalate. The composition of the obtained complex oxide was $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Sn}_{0.1}\text{O}_n$.

- Further, a gas phase catalytic reaction was conducted by supplying propane, ammonia and nitrogen in the same manner as in Example 24. The results are shown in Table 4.

EXAMPLE 27

- Using a complex oxide prepared in the same manner as in Example 9, a gas phase catalytic reaction was conducted by supplying propane, ammonia and nitrogen in the same manner as in Example 24. The results are shown in Table 4.

COMPARATIVE EXAMPLE 5

Using a complex oxide having the empirical composition $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_x$ prepared in the same manner as in Comparative Example 3, a gas phase catalytic reaction was conducted by supplying propane, ammonia and nitrogen in the same manner as in Example 24. The results are shown in Table 4.

Table 4

	Complex oxide (atomic ratio)	Conversion of propane (%)	Yield of acrylonitrile (%)
Example 24	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Fe}_{0.1}\text{O}_n$	12.5	5.3
Example 25	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Ti}_{0.1}\text{O}_n$	9.4	4.5
Example 26	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Sn}_{0.1}\text{O}_n$	11.7	5.7
Example 27	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Al}_{0.1}\text{O}_n$	12.3	5.6
Comparative Example 5	$\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{O}_n$	9.4	4.0

EXAMPLE 28

A complex oxide having the empirical composition $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{Pd}_{0.0008}\text{O}_n$ was prepared as follows.

In 117 ml of warm water, 4.21 g of ammonium metavanadate was dissolved, and 4.54 g of telluric acid, 15.89 g of ammonium paramolybdate and 1.4 ml of an aqueous palladium nitrate solution (concentration of Pd: 5.32 g/l) were sequentially added thereto to obtain a uniform aqueous solution. Further, 3.99 g of ammonium niobium oxalate was dissolved in 17.9 ml of water and added thereto. The aqueous solution thereby obtained was evaporated to dryness at about 150°C to obtain a solid material.

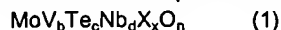
This solid material was molded into a tablet of 5 mm in diameter and 3 mm in length by a tableting machine, following pulverization and sieving to obtain a powder of from 16 to 28 mesh. The powder was calcined at a temperature of at least 350°C, and then used for the reaction.

0.5 ml of the complex oxide thus obtained, was charged into reactor, and a gas phase catalytic reaction was conducted at a reaction temperature of 440°C at a space velocity SV of 2000 hr⁻¹ by supplying a feed gas at a molar ratio of propane:ammonia:air = 1:1.2:10. As a result, the conversion of propane was 62.2%, the selectivity for acrylonitrile was 51.9%, and the yield of acrylonitrile was 32.3%.

According to the process of the present invention, by using a novel complex oxide while an alkane is used as the starting material, a desired nitrile can be produced in good yield at a relatively low temperature at a level of from 380 to 480°C without requiring the presence of a halide or water in the reaction system.

Claims

1. A process for producing a nitrile, which comprises subjecting an alkane and ammonia in the gaseous state to catalytic oxidation in the presence of an oxide of empirical formula:



wherein:

X is at least one of Mg, Ca, Sr, Ba, Al, Ga, Tl, In, Ti, Zr, Hf, Ta, Cr, Mn, W, Fe, Ru, Co, Rh, Ni, Pd, Pt, Zn, Sn, Pb, As, Sb, Bi, La and Ce;

b is from 0.01 to 1.0;

c is from 0.01 to 1.0;
d is from 0 to 1.0;
x is from 0.0005 to 1.0; and
n is a number such that the total valency of the metal elements is satisfied.

5

2. A process according to claim 1 wherein:

b is from 0.1 to 0.5;
c is from 0.05 to 0.4; and
x is from 0.005 to 0.6.

10

3. A process according to claim 1 or 2 which is carried out in the presence of molecular oxygen.

4. A process according to any one of the preceding claims wherein the alkane has from 1 to 4 carbon atoms.

5. A process according to claim 4 wherein the alkane is propane.

15

6. A process according to any one of the preceding claims wherein the ammonia is present in an amount of from 0.2 to 5 mols per mol of the alkane.

7. A process according to any one of the preceding claims which is carried out at a temperature of from 380 to 480°C.

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4144

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 318 295 (MITSUBISHI KASEI CORPORATION) * claims 1-8 *	1-7	C07C253/24 C07C255/08
D	& JP-A-2 000 257 (...) ---		
A	US-A-3 833 638 (W. R. KNOX ET AL) * claim 1 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07C
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 13 AUGUST 1992	Examiner Hans Kapteyn
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.92 (P0401)